

Dear Dr. Yool,

Please find below our listing of the changes in response to the reviewers' comments. We refer to our author comments at <https://doi.org/10.5194/gmd-2021-211-AC1> and <https://doi.org/10.5194/gmd-2021-211-AC2> for our detailed responses. A tracked-change version of the manuscript highlighting the insertions and deletions in the text has also been uploaded alongside the revised manuscript. We hope these changes will address the reviewer's comments.

Best regards,

Olivier Sulpis, on behalf of the authors

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## Revisions in response to comments by Anonymous Referee #1

The overall structure of the model is not described in detail. I could find only a few sentences, e.g., L130-132: 'equations composing RADI are based on CANDI, the method-of-lines code by Boudreau (1996b). Unlike the model of Boudreau (1996b), RADI does not solve a set of reactive-transport differential equations but instead computes the concentrations of a set of solids and solutes at each time step following a time vector set by the user.' Equations provided by the authors, however, indicate that they seem to use some time-forward finite difference method, e.g., L387: 'backward difference discretization prevails', and thus they seem to have governing differential equations from which difference equations are derived. If so, what is the difference from CANDI with respect to the general model structure including adopted numerical method?

It is somewhat disturbing to read that the model does not solve reactive-transport differential equations (L130-132), and correspondingly the authors did not provide any governing equations. A general reactive-transport equation (e.g., Boudreau, 1996, 1997) formulates the mass conservation law dictating that mass loss/gain via transport and reactions, and mass change within each sediment layer are balanced for each species. Thus, any model (including RADI) should end up in solving reactive-transport equations although the numerical approach can vary with models. Again, however, the numerical method and its difference (if any) from those of other models (including CANDI) are not clearly described in the text.

- **We added some text to section 2.1. and added two new equations describing the reactive-transport partial differential equations.**

In steady-state experiments, the authors used Muds to be compared with RADI (Sections 3.1 and 3.2). However, the comparison does not make any sense to me if RADI is tuned but Muds is not, to specific sites considered in this paper.

Also, the diagenetic influence of the updated rate law for CaCO<sub>3</sub> dissolution was discussed by comparing Muds and RADI (Section 3.4). This does not make any sense to me, either, given that ΣCO<sub>2</sub> and TALK production profiles from OM degradation can be different between the two models. If the authors want to discuss the effect of adopting the new rate law for calcite, they should compare two RADI simulations adopting the new and previous rate laws with individually tuned rate constants under otherwise the same boundary conditions.

- **We updated the text in section 3, Fig. 4 and Fig. 5. We do not use Muds anymore and instead compare two RADI simulations, one with ‘traditional’ and one with ‘new’ calcium carbonate kinetics.**

The authors argued that RADI can be used for simulations imposing an intense ocean acidification event such as PETM (Section 4.4), but one may doubt it. Under an intense dissolution event (such as PETM), chemical erosion can happen where burial velocity can become negative at certain sediment depths. However, the burial velocity calculation scheme of RADI does not seem to allow this (Eq. (14), Section 2.3 and Fig. 1). Indeed, given that burial calculation does not seem to reflect any mass/volume changes in solid species caused by reactions, the transient simulation of RADI should be limited to the cases where the effect of solid mass/volume changes on burial rate is minor, e.g., short term experiments with minor changes in solid phase concentrations such as those in Sections 4.1-4.3. To enable the application to cases involving a significant CaCO<sub>3</sub> dissolution, RADI has to adopt a different burial velocity calculation scheme, such as that adopted by Munhoven (2021, GMD, 14, 3603).

- **In section 4.4., we deleted the mention to the PETM and added some text to explain that a different burial velocity calculation scheme would need to be implemented to deal with long term major dissolution events.**

Fig. 1. Sediment layer/point numbers within the model domain and depths assigned to sediment layers/points seem to be confused. For example, in Fig. 1 Z looks like the total number of sediment points/layers meanwhile it is defined as the total sediment thickness in Table 1 and text. The same goes to dz.

- **We updated Fig. 1 to reflect definitions given in the text.**

L131-132. Quite vague description of the model. It is unclear how the model is different from or similar to CANDI (please also see general comment 1).

- **We added some text to section 2.1. and added two new equations describing the reactive-transport partial differential equations.**

L141. Is the threshold for dz/dt for stability of the numerical solution dependent on w?

- **No change required.**

L354. Is 30% d-1 the most used rate constant with the reaction order of 4.5? I thought 100% d-1 is more often adopted in the literature (e.g., Archer, 1991, 1996; Archer et al., 1996).

- **We changed the rate constant to 100% d<sup>-1</sup> and have updated the text, the figures, and the model simulations presented in section 3 to reflect this new value.**

Eqs. (11)-(14). What is the difference between x and w? Also, in Eq. (13) porewater volume fraction should be used instead of solid volume fraction. How do you calculate  $w_{\infty}$  and  $u_{\infty}$ ? I guess the authors assume  $w_{\infty} = u_{\infty} = x_{\infty}$ ?

- **We changed the text and equations in section 2.3 to correct for the mistakes pointed out to by the reviewer.**

Section 3.1. It does not make any sense to compare 2 models if the 2 models are not tuned to the observations in the same way (only RADI is tuned and Muds is not tuned?). If the rate constants and/or

rate laws are different between the two models, I would expect different boundary conditions for 2 different tuned models.

- **We updated the text in section 3, Fig. 4 and Fig. 5. We do not use Muds anymore and instead compare two RADI simulations, one with ‘traditional’ and one with ‘new’ calcium carbonate kinetics.**

L528-530. Is the assumption to calculate DBL thickness by Sulpis et al. (2018) consistent with RADI’s assumption? In other words, isn’t the calculation of DBL thickness by Sulpis et al. (2018) affected by including CaCO<sub>3</sub> dissolution by OM-derived CO<sub>2</sub>?

- **No change required.**

L549. The good reproduction of NO<sub>3</sub> profile seems to be achieved at the cost of bad OM profile reproduction, for which Muds does seem to do a better job. I think the same goes to the O<sub>2</sub> profile difference between the two models

- **No change required.**

Fig. 4. Calcite concentration does not seem to increase at the bottom, which looks weird given the oversaturation of calcite at the bottom and assuming that RADI allows for precipitation.

- **We added a new sentence at the end of section 3.1 discussing the calcite increase at the bottom.**

Section 3.2. The issues raised for Section 3.1 can apply to Section 3.2. L649. I guess the authors can definitely tell by repeating the same tuning experiments with RADI adopting the rate law used by Muds. (Please also see general comment 2.) Could you attribute some of differences in CO<sub>2</sub> and TALK profiles to the difference in OM diagenesis schemes between the models?

- **We updated the text in section 3, Fig. 4 and Fig. 5. We do not use Muds anymore and instead compare two RADI simulations, one with ‘traditional’ and one with ‘new’ calcium carbonate kinetics.**

Fig. 8. How can it be possible that O<sub>2</sub> and CO<sub>2</sub> fluctuate while OM and CaCO<sub>3</sub> do not? Is the magnitude of fluctuation of OM and CaCO<sub>3</sub> too small to see in the figure?

- **No change required.**

Section 4.3. Why changes in OM degradation and CaCO<sub>3</sub> dissolution are significant while no changes are recognized in Section 4.2? Is this only because imposed DBL changes are larger in Section 4.3? Or is the response of sedimentary system to DBL change dependent on the time rate of DBL change imposed?

- **We edited Fig. 9 which was not labelled properly.**

L71. ‘Cappellen’ should be ‘Van Cappellen’

- **We changed that.**

Table 1 and throughout. Although the authors stated that variables are written in italic and model notations are in monospaced font (L93), this rule is not completely followed.

- **We updated Table 1.**

## Revisions in response to comments by Dr. Burdige

The second is that the model is explicitly discussed in the context of its ability to look at time dependent problems. Strictly speaking, this is not exactly new since other models out there (e.g., CANDI) can, in principle, also be used to examine time-dependent problems. However, these models generally are not used in this fashion and the work shown here presents some interesting observations based on time-dependent simulations using RADI.

A concern I have, though, about the model is that they use total alkalinity and total DIC as solute variables, rather than calculating them from individual chemical components (I know this is touted as an advantage of this model, but I'm not as convinced that it really is). Given that a major thrust of this work is examining carbonate dissolution in deep-sea sediments this seems like a possible problem. Rather than calculating  $[H^+]$  and  $[CO_3^{2-}]$  from Alk and DIC profiles (see line 297) wouldn't it make more sense to model  $H^+$  and carbonate (or bicarbonate) concentrations directly in the model and then calculate alkalinity and DIC depth profiles at the end of each time step. Such a model would be just as easy to use as RADI is in terms of comparing model results with field observations and would likely be more accurate. This would probably also require the addition of an equation for borate in the model, but that would be an easy addition (see, for example, the approaches described in Hoffmann et al. [Biogeosci. 5, 227-251, 2008] and Faber et al. [Biogeosci. 9, 4087-4097, 2012]).

Maybe I'm missing something, but since one of the major efforts here is to more realistically quantify carbonate dissolution in early diagenetic models the approach taken in RADI to "directly" model Alkalinity and DIC as solute variables seems like it adds unnecessary uncertainty. It also requires that they use the bicarbonate diffusion coefficient for DIC and alkalinity (line 395), which adds further uncertainty in the calculation of carbonate ion concentration gradients and fluxes near the sediment surface, which is where most calcium carbonate dissolves in the deep sea.

- **We added one new discussion section in the supplement ("Using TAlk and  $\Sigma CO_2$  as solute variables, rather than their individual components"), one supplementary figure (Fig. S2), some text and two new equations in section 2.2.3. We have also added a sentence in section 2.4 discussing this and referring to Fig. S2.**

(130-1) – Just so I'm clear, the "diagenetic equations" in RADI are still differential equations (also see the next comment) + (132) – How exactly does RADI compute "the concentrations of a set of solids and solutes at each time step"? This should be briefly discussed here and perhaps presented in a bit more detail in the supporting information section. Also, in addition to describing these equations part-by-part in the text it might be nice to present some sort of summary of the complete equations in the supporting information section. Perhaps only modeling "geeks" like me would want to see this, but I think it would be good for this to be available, should any reader be so interested in seeing this information.

- **We added some text to section 2.1. and added two new equations describing the reactive-transport partial differential equations, we have also added a new supplementary section ("Full RADI equations").**

(181) – Why and how is Clay being modeled here? This is never really discussed (unless I missed it).

- **We added a sentence precisizing that at the end of section 2.1.**

(228) - What exactly is meant by "the reactivities decline with depth"? I'm assuming the  $k$ 's in eqn. (4) are constants for a given site (since based on eqns. (7a) and (7b) they only depend on the carbon rain rate

to the sediment), so the overall rate of organic matter degradation at any given site should decrease with depth solely because of changes with depth in the quantity of organic matter and the relative proportions of fast and slow decay materials that are present. Am I missing something here?

- **We edited that part of the text in section 2.2.1 and deleted the mention that reactivities decrease with depth.**

(250) – Is there a subscript “z” missing for the k on this line?

- **We edited equations (6), (9a) and (9b).**

(268) – “This scheme ...” - I would think that the way alkalinity and DIC are modeled in RADI will also make it difficult to apply this model to coastal and anoxic sediments

- **We added a sentence at the end of section 5 to make this point.**

(299) – How are the concentrations of fluoride, borate and silicate obtained?

- **We updated the text in section 2.2.3 to remove the mention to fluoride and explain where borate and silicate concentrations are taken from.**

(307) – It’s not clear to me how the reaction order ( $\eta$ ) implicitly accounts for each carbonate mineral’s specific surface area. The discussion later on only talks about how the reaction order varies with  $\Omega$ .

- **We rephrased that sentence to clarify.**

In the caption to Fig. 2 it states that calcite and aragonite dissolution rates are based on eqns. (8) and (9) but it isn't until you read a little further that you learn that  $\eta$  is actually a complex function of  $\Omega$  (starting on line 334). It might be good to at least mention this in the figure caption.

- **We clarified that in the figure caption.**

Fig. 4 has two different types of symbols in the O<sub>2</sub> profiles. I think I figured out the differences from reading the text (lines 547-548), but this should be clarified in the figure legend and/or caption

- **We clarified that in the legend.**

(583) – “in the laboratory” but on-board ship? Please clarify.

- **We clarified that in the sentence.**

(704) - Will tides in the deep sea (water depth 4370 at station #W-2) really generate this large a change in DBL thickness (i.e., from 0.5 to 3.5 mm)?

- **We changed those values to reflect those that were used in the simulation and in Fig. 8, that span a narrower, more realistic range.**

(715) – Tides affect both the concentration gradient at the sediment water interface as well as the thickness of the DBL, so the combined effects should then impact the benthic flux. Do these two factors reinforce one another, cancel each other out, or do something in-between? Some of these issues are alluded to indirectly in the next section (4.3), but I wonder if this is worth looking at and/or considering here more explicitly.

- **No change required.**

(753) – I would say “a 5-fold decrease in  $\delta$ ”.

- **We changed that.**

(760-1) – “... the quick adjustment of porewater concentrations to the new diffusive boundary layer ...” – Might it be worth showing these profiles (perhaps in the supporting information section)?

- **We added these profiles in a new figure in the supplementary information (Fig. S3).**

9 – Please define which color goes with which solute. I’m assuming blue is oxygen, but this (and the other colors) should be explicitly labelled.

- **We updated Fig. 9.**

(781) – I think that trying to model carbon isotopes from POC degradation will be challenging if you use a reactive continuum approach, even if this approach is more appropriate for many studies. In part, that is why we use a similar “multi-G” approach to the one used here in our work modeling POC, DIC and DOC degradation in sediments (both total C,  $^{13}\text{C}$  and  $^{14}\text{C}$ )

- **We have deleted the sentence mentioning a reactive continuum approach.**

(787) – As noted above, I wonder if applications of the RADI model to coastal sediments will be difficult given the way alkalinity and DIC are being modelled here

- **We added a sentence at the end of section 5 to make this point.**